

Construction and counting of the number operators of an n -degree-of-freedom normalized non-resonant vibrational Hamiltonian

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Abstract

The present paper is the first of two articles aimed at constructing n -degree-of-freedom Hamiltonian systems by an algebraic approach. In molecular spectroscopy, the construction of vibrational Hamiltonian for strongly excited molecular systems by using an algebraic formalism requires the introduction by hand the operators describing the change in energy by numerous quanta and it is tedious to predict in advance the total number of operators appearing in the development. The goal of the two articles is not only to propose in the local limit a systematic method for constructing a normalized vibrational Hamiltonian for a strongly excited n -degree-of-freedom molecular system from the generators of the Lie algebra, the algebra of polynomial invariants, but also to enumerate the number of independent operators needed for the construction of the Hamiltonian developed in the base of these generators up to the given order N . The first article introduces the theoretical tools used in the both papers (section 2), and presents the method of construction in case of absence of resonance (section 3). Finally, an application for a triatomic non-linear ClOH molecule is considered in case close to the dissociation limit. (section 4).

Keywords: Molecular structure ; Vibrational Hamiltonian ; Lie Algebra ; Polynomial Invariants.

1. Introduction

Since years 1990, algebraic formalisms are developed in molecular spectroscopy (e.g. [1], [2]). For instance, the vibrational structure of local stretching modes for tetrahedral molecules AB₄ has been studied through algebraic chains by ([3]). To model molecular vibrations the theory of local modes (e.g. [4, 5]) associates for each of n degrees of freedom in vibration an oscillator to each bond and to each angular deformation. When molecular systems are strongly excited or they are highly anharmonic already at small quantum numbers, this description corresponds to a treatment that is more adequate for vibrational modes

than for the normal ones.

In classical mechanics the study around a fixed point consists in writing the Hamiltonian \mathcal{H} as a power series expansion of ϵ (ϵ is a non-dimensional parameter small compared to 1 and the different Hamiltonians appearing in the development are of the same order, and the development is up to the order \tilde{N} , with \tilde{N} being non-zero integer): $\mathcal{H} \approx \mathcal{H}_0 + \sum_{k=1}^{\tilde{N}} \epsilon^k \mathcal{H}_k$, \mathcal{H}_0 being the Hamiltonian describing the system up to the lowest order and \mathcal{H}_k ($k = 1, \dots, \tilde{N}$) are the perturbation Hamiltonians. It follows from this equation that \mathcal{H}_0 is not rigorously the first integral for the studied system.

Birkhoff ([6]) then Gustavson ([7]) or Deprit ([8]) proposed a so-called procedure of normalisation to a new Hamiltonian \mathcal{K} having a simpler form than \mathcal{H} , called nor-

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malized Hamiltonian, and commuting with \mathcal{H}_0 in the sense of Poisson irregardless of the order up to which it is developed. Just like \mathcal{H} , the normalized Hamiltonian can be written as a power series development of ϵ ; for the development up to the order \tilde{N} , we have: $\mathcal{K} \approx \mathcal{H}_0 + \sum_{k=1}^{\tilde{N}} \epsilon^k \mathcal{K}_k$. In this article, we consider the so-called standard normalisation ([9]) of n -degree-of-freedom harmonic oscillator, i.e. the Hamiltonian of the lowest order \mathcal{H}_0 is a polynomial of the second order in dynamic variables and reads: $\mathcal{H}_0 = \sum_{k=1}^n \frac{\omega_k(q_k^2 + p_k^2)}{2}$, with ω_k being the frequencies ($1 \leq i, j \leq n$, $\omega_i \neq \omega_j$).

2. Normalisation

2.1. Hamiltonian of the lowest order: \mathcal{H}_0

Let $\mathcal{H}(q_1, \dots, q_n, p_1, \dots, p_n)$ be the classical vibrational Hamiltonian of an n -degree-of-freedom Hamiltonian system with the quadratic part being that of an anisotropic harmonic oscillator $\mathcal{H}_0 = \sum_{k=1}^n \frac{\omega_k(q_k^2 + p_k^2)}{2}$, where ω_k are frequencies ($1 \leq i, j \leq n$, $\omega_i \neq \omega_j$) and q_k and p_k are the non-dimensional canonical variables describing the generalized coordinates and their conjugated momenta.

2.2. Equation of motion

We introduce here the complex variables z_k and z_k^* defined as functions of canonical variables q_k and p_k ($k \in [1, \dots, n]$) $z_k = \frac{1}{\sqrt{2}}(q_k + ip_k)$ and $z_k^* = \frac{1}{\sqrt{2}}(q_k - ip_k)$. These variables satisfy the relations: $1 \leq j, k \leq n$, $\{z_j, z_k^*\} = \sum_{i=1}^n (\frac{\partial z_j}{\partial q_i} \frac{\partial z_k^*}{\partial p_i} - \frac{\partial z_j}{\partial p_i} \frac{\partial z_k^*}{\partial q_i}) = -i\delta_{jk}$. The change of coordinates from (q_k, p_k) to (z_k, z_k^*) is a symplectic transformation of multiplier $-i$. The Hamiltonian \mathcal{H}_0 reads: $\mathcal{H}_0 = -i \sum_{k=1}^n \omega_k z_k z_k^*$. In complexes coordinates, for $1 \leq k \leq n$, the equations of motion are:

$$\frac{dz_k}{dt} = \frac{\partial \mathcal{H}_0}{\partial z_k^*} = -i\omega_k z_k. \quad (1)$$

2.3. Hamiltonian flow

For an initial condition $z_0 = (z_{1,0}, \dots, z_{n,0})$, the solution to the equation of motion is written formally as

$z(t) = \phi_t^{\mathcal{H}_0}(z_0)$. The application $\phi_t^{\mathcal{H}_0} : \Gamma \rightarrow \Gamma$ is the Hamiltonian flow generated ([10, 11]) by \mathcal{H}_0 .

$$\text{We have: } z(t) = \phi_t^{\mathcal{H}_0}(z_0) \implies \begin{pmatrix} z_1(t) \\ \vdots \\ z_n(t) \end{pmatrix}$$

$$= \begin{pmatrix} e^{-i\omega_1 t} & 0 & \dots & 0 \\ 0 & e^{-i\omega_2 t} & \dots & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & e^{-i\omega_n t} \end{pmatrix} \begin{pmatrix} z_{1,0} \\ \vdots \\ z_{n,0} \end{pmatrix}. \quad (2)$$

The solutions $z(t)$ still constitute the trajectories of the Hamiltonian flow or the orbits of the harmonic oscillator.

2.4. Normalisation tools

2.4.1. Mathematical condition of non-resonance

The Hamiltonian \mathcal{H}_0 is called non-resonant (for example [12]) if the n frequencies ω_k are independents, i.e. (λ_k are all zero integers):

$$\sum_{k=1}^n \lambda_k \omega_k = 0. \quad (3)$$

2.4.2. Adjoint operator $ad_{\mathcal{H}_0}$

The adjoint operator associated to Hamiltonian \mathcal{H}_0 is the linear operator acting in the phase space Γ ([13]) $ad_{\mathcal{H}_0} : \forall \mathcal{G} \in \Gamma, \mathcal{G} \rightarrow ad_{\mathcal{H}_0}(\mathcal{G}) = \{\mathcal{G}, \mathcal{H}_0\} = \sum_{i=1}^n \left(\frac{\partial \mathcal{G}}{\partial q_i} \frac{\partial \mathcal{H}_0}{\partial p_i} - \frac{\partial \mathcal{G}}{\partial p_i} \frac{\partial \mathcal{H}_0}{\partial q_i} \right)$. In complex coordinates, this operator reads:

$$ad_{\mathcal{H}_0} = \sum_{k=1}^n \omega_k \left(z_k^* \frac{\partial}{\partial z_k^*} - z_k \frac{\partial}{\partial z_k} \right). \quad (4)$$

2.4.3. Sets $Ker ad_{\mathcal{H}_0}$ and $Im ad_{\mathcal{H}_0}$

The complex monomials $\sigma = z_1^{\alpha_1} z_1^{*\beta_1} \dots z_n^{\alpha_n} z_n^{*\beta_n}$ (with $\sum_{k=1}^n (\alpha_k + \beta_k) = m$ being the monomial degree, and α_k and β_k being integers) are the elements of the complex polynomials circle $\mathbb{C}(z, z^*)$ and are the eigenvectors of $ad_{\mathcal{H}_0}$ as:

$$ad_{\mathcal{H}_0}(\sigma) = \left(\sum_{k=1}^n \omega_k (\beta_k - \alpha_k) \right) (\sigma). \quad (5)$$

$Ker ad_{\mathcal{H}_0}$ (kernel of $ad_{\mathcal{H}_0}$) and $Im ad_{\mathcal{H}_0}$ (image of $ad_{\mathcal{H}_0}$) verify (resp.) $ad_{\mathcal{H}_0}(\sigma) = 0$ and $ad_{\mathcal{H}_0}(\sigma) \neq 0$.

2.4.4. Circles of complex polynomials invariant with the time reversal

The application of the time reversal operator τ on the set (z_k, z_k^*) ($1 \leq k \leq n$) gives: $\tau(z_k) = z_k^*$, $\tau(z_k^*) = z_k$. We denote by $\mathbb{C}(z, z^*)^\tau$ the sub-circle of the monomials σ invariant with respect to the time reversal ([14]): $\mathbb{C}(z, z^*)^\tau = \{\sigma \in \mathbb{C}(z, z^*) / \tau(\sigma) = \sigma\}$.

2.4.5. Hilbert base

Due to the condition of non-resonance (3), the kernel of adjoint operator $ad_{\mathcal{H}_0}$ is produced (created) by the n monomials $\sigma_1 = z_1 z_1^*$, ..., $\sigma_n = z_n z_n^*$ all belonging to $\mathbb{C}(z, z^*)^\tau$. $Ker\ ad_{\mathcal{H}_0}$ has a Lie algebra structure called algebra of invariant polynomials. The generators σ_k ($1 \leq k \leq n$) form a base of $Ker\ ad_{\mathcal{H}_0}$ called Hilbert base ([15, 16, 17]). This base is unique for a non-resonant Hamiltonian ([13]).

The generators are invariants with respect to flow of the harmonic oscillator, i.e.: $\forall t, 1 \leq k \leq n, \forall z \in \Gamma$,

$$\sigma_k(\phi_t^{\mathcal{H}_0}(z)) = \sigma_k(z). \quad (6)$$

(6) means that $\phi_t^{\mathcal{H}_0}$ is a symplectic symmetry for the generators of the algebra ([10, 11, 12]); in other terms, according to the Noether theorem, $1 \leq k \leq n$, $\{\sigma_k, \mathcal{H}_0\} = 0$.

Reciprocally, we know that by construction the generators σ_k belong to $Ker\ ad_{\mathcal{H}_0}$, so $1 \leq k \leq n$, $\{\sigma_k, \mathcal{H}_0\} = 0$. If \mathcal{H}_0 is an invariant for the generators then, according to the "reciprocity" of the Noether theorem, $\phi_t^{\mathcal{H}_0}$ is a symplectic symmetry for the generators. Thus we have :

$$\begin{aligned} \forall t, 1 \leq k \leq n, \forall z \in \Gamma, \sigma_k(\phi_t^{\mathcal{H}_0}(z)) &= \sigma_k(z), \\ \iff \{\sigma_k, \mathcal{H}_0\} &= 0. \end{aligned} \quad (7)$$

In complex coordinates, the Poisson brackets between the generators read (pour $1 \leq i, j \leq n$):

$$\{\sigma_i, \sigma_j\} = i \sum_{k=1}^n \left(\frac{\partial \sigma_i}{\partial z_k^*} \frac{\partial \sigma_j}{\partial z_k} - \frac{\partial \sigma_i}{\partial z_k} \frac{\partial \sigma_j}{\partial z_k^*} \right) = 0. \quad (8)$$

2.4.6. Normalized Hamiltonian \mathcal{K}

We look for constructing a Hamiltonian called normalized Hamiltonian \mathcal{K} such that \mathcal{H}_0 commute with \mathcal{K} ,

i.e. $\{\mathcal{H}_0, \mathcal{K}\} = -ad_{\mathcal{H}_0}(\mathcal{K}) = ad_{\mathcal{K}}(\mathcal{H}_0) = 0$. The normalized Hamiltonian has the following form ([13]): $\mathcal{K} = \mathcal{H}_0 + f(\sigma_1, \dots, \sigma_n)$. As the generators of the Hilbert base are invariant with respect to the time reversal, the Hamiltonian is invariant as well: $\tau(\mathcal{K}) = \mathcal{K}$.

2.4.7. Order of the development

In two articles, we write the normalized Hamiltonian as a power polynomial development of the generators. In what follows, we denote by λ -monomial of degree $d = \sum_{\ell=1}^{\lambda} 2r_{i_\ell}$ each monomial formed by the product of the powers of λ generators of the Hilbert base ($2 \leq \lambda \leq n$): $\sigma_{i_1}^{r_{i_1}} \dots \sigma_{i_\lambda}^{r_{i_\lambda}}$ (obviously $d \geq 2\lambda$). The order N of the development is fixed by the λ -monomials of the highest degree $d = N$ of the Hamiltonian \mathcal{K} . In the first article as the generators of the Hilbert base are all of the order 2, the order N is necessarily pair (with $N \geq 2$).

3. Construction of counting

3.1. Case $n = 2$

3.1.1. Construction of the normalized Hamiltonian

This case can model, for example, the two stretching local modes of rigid triatomic linear molecules ABC, and also all molecular systems having at least two vibrational non-resonant modes.

The normalized non-resonant Hamiltonian \mathcal{K} , with the quadratic part $\mathcal{H}_0 = -i(\omega_1 \sigma_1 + \omega_2 \sigma_2)$, is only the function of σ_1 et σ_2 : $\mathcal{K} = \mathcal{H}_0 + f(\sigma_1, \sigma_2)$.

Let us write it down as a polynomial development of σ_1 and σ_2 up to the order N ($N \geq 4$ is natural integer):

$$\begin{aligned} \mathcal{K} &= \mathcal{H}_0 + \sum_{q_0=2}^{Q_0} (\alpha_{q_0}^1 \sigma_1^{q_0} + \alpha_{q_0}^2 \sigma_2^{q_0}) \\ &+ \sum_{r=2}^{Q_0} \sum_{1 \leq i_1 < i_2 \leq 2} \sum_{r_{i_1} \geq 1, r_{i_2} \geq 1}^{r_{i_1} + r_{i_2} = r} \alpha_{r_{i_1}, r_{i_2}}^{i_1, i_2} \sigma_{i_1}^{r_{i_1}} \sigma_{i_2}^{r_{i_2}}. \end{aligned} \quad (9)$$

In Eq. (9), the monomials are all real. Moreover, the transformation of (q_k, p_k) to (z_k, z_k^*) is a symplectic transformation of multiplier $-i$, in the manner of the Hamiltonian \mathcal{K} , we deduce that all the coefficients $\alpha_{q_0}^1, \alpha_{q_0}^2, \alpha_{r_{i_1}, r_{i_2}}^{i_1, i_2}$

are pure imaginary; q_0, i_1, i_2, r_{i_1} and r_{i_2} are natural integers; in (9), the degree d of the monomials $\sigma_1^{q_0}, \sigma_2^{q_0}$ and $\sigma_{i_1}^{r_{i_1}} \sigma_{i_2}^{r_{i_2}}$ is equal to $2q_0$ and $2r$, respectively; q_0 and r take all the integer values from 2 to a maximal value Q_0 such that $Q_0 = E(\frac{N}{2})$ with $E(x)$ being the integer (entire) part of x . If $N = 2$, the coefficients $\alpha_{r_{i_1}, r_{i_2}}^{i_1, i_2}, \alpha_{q_0}^1$ and $\alpha_{q_0}^2$ are zero. Moreover, \mathcal{K} contains $\frac{Q_0(Q_0+3)}{2}$ monomials.

3.1.2. Independence of the coefficients

Let us write down the Jacobi equality ($1 \leq j \leq 2$): $\{\mathcal{K}, \{\sigma_j, \mathcal{H}_0\}\} + \{\mathcal{H}_0, \{\mathcal{K}, \sigma_j\}\} + \{\sigma_j, \{\mathcal{H}_0, \mathcal{K}\}\} = 0$. Calculating the different Poisson brackets $\{\mathcal{K}, \sigma_j\}$ and knowing that $(\mathcal{K}, \sigma_j) \in \text{Ker } \text{ad}_{\mathcal{H}_0}$, we deduce that there is no relation between the coefficients of the development of Eq. (9): the different λ -monomials are independent between them. The Hamiltonian is described by as many monomials as the coefficients.

3.2. Case $n = 3$

This mathematical study can be used as a model, for example, for rigid molecules to describe local modes (stretching or bending) of triatomic non linear molecules, ABC or AB₂.

The normalized non-resonant Hamiltonian \mathcal{K} with the quadratic part $\mathcal{H}_0 = -i(\omega_1\sigma_1 + \omega_2\sigma_2 + \omega_3\sigma_3)$ is only the function of σ_1, σ_2 and σ_3 : $\mathcal{K} = \mathcal{H}_0 + f(\sigma_1, \sigma_2, \sigma_3)$.

Let us write down it as a polynomial development of σ_1, σ_2 and σ_3 up to the order N :

$$\mathcal{K} = \mathcal{H}_0 + \sum_{q_0=2}^{Q_0} (\alpha_{q_0}^1 \sigma_1^{q_0} + \alpha_{q_0}^2 \sigma_2^{q_0} + \alpha_{q_0}^3 \sigma_3^{q_0}) + \sum_{\ell=2}^3 \sum_{r=2}^{Q_0} \sum_{1 \leq i_1 < \dots < i_\ell \leq 3} \sum_{r_{i_1} \geq 1, \dots, r_{i_\ell} \geq 1}^{r_{i_1} + \dots + r_{i_\ell} = r} \alpha_{r_{i_1}, \dots, r_{i_\ell}}^{i_1, \dots, i_\ell} \sigma_{i_1}^{r_{i_1}} \dots \sigma_{i_\ell}^{r_{i_\ell}}. \quad (10)$$

i_1, \dots, i_ℓ are non-zero natural integers satisfying the order relations: $1 \leq i_1 < \dots < i_\ell \leq 3$; $r_{i_1}, \dots, r_{i_\ell}$ are non-zero natural integers satisfying the relation $r_{i_1} + \dots + r_{i_\ell} = r$, with r being the natural integer comprised between 2 and

Q_0 . The coefficients $\alpha_{q_0}^k$ ($1 \leq k \leq 3$), $\alpha_{r_{i_1}, \dots, r_{i_\ell}}^{i_1, \dots, i_\ell}$ are the pure imaginary parameters. For $N < 6$ all the terms of the last summation of the rhs of Eq. (10) are identically equal to zero. Besides, \mathcal{K} contains $\frac{Q_0(Q_0^2+Q_0+11)}{6}$ monomials.

3.3. General case

3.3.1. Construction of the normalized Hamiltonian

The quadratic part of the normalized non-resonant Hamiltonian \mathcal{K} reads: $\mathcal{H}_0 = -i \sum_{k=1}^n \omega_k \sigma_k$. The n quantities ω_k are the characteristic frequencies of the oscillators.

Let us write \mathcal{K} as a function of n generators of the Hilbert base: $\mathcal{K} = \mathcal{H}_0 + f(\sigma_1, \dots, \sigma_n)$.

In case of absence of resonance between two any oscillators, let us write down \mathcal{K} as a polynomial development (development of Dunham) of $\sigma_1, \sigma_2, \dots, \sigma_n$ (with $n \geq 3$ being natural integer) up to the order N :

$$\mathcal{K} = \mathcal{H}_0 + \sum_{k=1}^n \sum_{q_0=2}^{Q_0} \alpha_{q_0}^k \sigma_k^{q_0} + \sum_{\ell=2}^n \sum_{r=2}^{Q_0} \sum_{1 \leq i_1 < i_2 < \dots < i_\ell \leq n} \sum_{r_{i_1} \geq 1, \dots, r_{i_\ell} \geq 1}^{r_{i_1} + \dots + r_{i_\ell} = r} \alpha_{r_{i_1}, \dots, r_{i_\ell}}^{i_1, \dots, i_\ell} \sigma_{i_1}^{r_{i_1}} \dots \sigma_{i_\ell}^{r_{i_\ell}}. \quad (11)$$

i_1, \dots, i_ℓ are the non-zero natural integers satisfying the order relations : $1 \leq i_1 < i_2 < \dots < i_\ell \leq n$; $r_{i_1}, \dots, r_{i_\ell}$ are the non-zero natural integers satisfying a relation $r_{i_1} + \dots + r_{i_\ell} = r$, with r being a natural integer comprised between 2 and Q_0 . The coefficients $\alpha_{q_0}^k$ and $\alpha_{r_{i_1}, \dots, r_{i_\ell}}^{i_1, \dots, i_\ell}$ are the pure imaginary parameters. For $N < 6$, all the terms of the last summation of the rhs of Eq. (11) are identically equal to zero. Proceeding as in Section 3.1.2, we verify that all the λ -monomials in Eq. (11) are independent.

3.3.2. Counting

The counting of the number Λ of independent operators required to construct \mathcal{K} for the case $n = 3$ can be presented in the form ($N \geq 6$):

$$\begin{aligned} \Lambda &= 3 + 3(Q_0 - 1) + \frac{3Q_0(Q_0 - 1)}{2} \\ &\quad + \frac{Q_0(Q_0 - 1)(Q_0 - 2)}{6}, \\ \Lambda &= \sum_{\lambda=1}^3 C_3^\lambda C_{Q_0}^\lambda. \end{aligned} \quad (12)$$

Let us generalize the counting formula (12) for an n -degree-of-freedom system ($n \geq 3$).

For the order N and d data ($2\lambda \leq d \leq N$), there is C_n^λ ways of choosing the λ generators of a λ -monomial of degree d among the set $(\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_n)$. Moreover, for a given choice of λ generators, let us denote by N_r the number of ways to realize a λ -monomial $\sigma_{i_1}^{r_{i_1}} \dots \sigma_{i_\lambda}^{r_{i_\lambda}}$, with the set of powers $(r_{i_1}, \dots, r_{i_\lambda})$ that should satisfy, in accordance to Eq. (11), the condition $r_{i_1} + \dots + r_{i_\lambda} = r$. Note that $C_{Q_0}^\lambda = \sum_{r=\lambda}^{Q_0} N_r$. We deduce from this that for the given N and λ , there is $C_n^\lambda C_{Q_0}^\lambda$ independent monomials entering the composition of \mathcal{K} . Finally, as the maximal value of λ is fixed either by the number of the degree of freedom of the Hamiltonian system if $Q_0 \geq n$, or either by Q_0 if $Q_0 \leq n$, the total number of independent monomials in \mathcal{K} is obtained by adding the $C_n^\lambda C_{Q_0}^\lambda$ of $\lambda = 1$ to the smallest value of n or Q_0 : $\min(n, Q_0)$. It follows that \mathcal{K} contains:

$$\Lambda = \sum_{\lambda=1}^{\min(n, Q_0)} C_n^\lambda C_{Q_0}^\lambda \text{ monomials.} \quad (13)$$

As an example, Table 1 shows, for $n = 3$ and $n = 4$ the number of monomials Λ in \mathcal{K} developed up to the order $N = 8$, as well as the list of monomials.

The case $n = 4$ can describe, for rigid molecules, two stretching non-resonant local modes and two non-resonant bending modes of tetrahedral molecules AB_3C .

4. Application

4.1. Molecule ClOH ($n = 3$)

4.1.1. Conventions of notation

The molecule ClOH is a triatomic non-linear molecule of 3 vibrational degrees of freedom ($n = 3$). In the local limit, we attach a stretching oscillator to bond Cl-O (oscillator "1") and O-H (oscillator "3") and a bending oscillator to the angle between these bonds (oscillator "2").

n	Λ	monomials
3	34	$\sigma_1, \sigma_2, \sigma_3$ $\sigma_1^2, \sigma_2^2, \sigma_3^2, \sigma_1^3, \sigma_2^3, \sigma_3^3, \sigma_1^4, \sigma_2^4, \sigma_3^4$ $\sigma_1\sigma_2, \sigma_1^2\sigma_2, \sigma_1\sigma_2^2, \sigma_1^3\sigma_2, \sigma_1^2\sigma_2^2, \sigma_1\sigma_2^3$ $\sigma_1\sigma_3, \sigma_1^2\sigma_3, \sigma_1\sigma_3^2, \sigma_1^3\sigma_3, \sigma_1^2\sigma_3^2, \sigma_1\sigma_3^3$ $\sigma_2\sigma_3, \sigma_2^2\sigma_3, \sigma_2\sigma_3^2, \sigma_2^3\sigma_3, \sigma_2^2\sigma_3^2, \sigma_2\sigma_3^3$ $\sigma_1\sigma_2\sigma_3, \sigma_1^2\sigma_2\sigma_3, \sigma_1\sigma_2^2\sigma_3, \sigma_1\sigma_2\sigma_3^2$
4	69	$\sigma_1, \sigma_2, \sigma_3, \sigma_4$ $\sigma_1^2, \sigma_2^2, \sigma_3^2, \sigma_4^2, \sigma_1^3, \sigma_2^3, \sigma_3^3, \sigma_4^3, \sigma_1^4, \sigma_2^4, \sigma_3^4, \sigma_4^4$ $\sigma_1\sigma_2, \sigma_1^2\sigma_2, \sigma_1\sigma_2^2, \sigma_1^3\sigma_2, \sigma_1^2\sigma_2^2, \sigma_1\sigma_2^3$ $\sigma_1\sigma_3, \sigma_1^2\sigma_3, \sigma_1\sigma_3^2, \sigma_1^3\sigma_3, \sigma_1^2\sigma_3^2, \sigma_1\sigma_3^3$ $\sigma_1\sigma_4, \sigma_1^2\sigma_4, \sigma_1\sigma_4^2, \sigma_1^3\sigma_4, \sigma_1^2\sigma_4^2, \sigma_1\sigma_4^3$ $\sigma_2\sigma_3, \sigma_2^2\sigma_3, \sigma_2\sigma_3^2, \sigma_2^3\sigma_3, \sigma_2^2\sigma_3^2, \sigma_2\sigma_3^3$ $\sigma_2\sigma_4, \sigma_2^2\sigma_4, \sigma_2\sigma_4^2, \sigma_2^3\sigma_4, \sigma_2^2\sigma_4^2, \sigma_2\sigma_4^3$ $\sigma_3\sigma_4, \sigma_3^2\sigma_4, \sigma_3\sigma_4^2, \sigma_3^3\sigma_4, \sigma_3^2\sigma_4^2, \sigma_3\sigma_4^3$ $\sigma_1\sigma_2\sigma_3, \sigma_1^2\sigma_2\sigma_3, \sigma_1\sigma_2^2\sigma_3, \sigma_1\sigma_2\sigma_3^2$ $\sigma_1\sigma_2\sigma_4, \sigma_1^2\sigma_2\sigma_4, \sigma_1\sigma_2^2\sigma_4, \sigma_1\sigma_2\sigma_4^2$ $\sigma_1\sigma_3\sigma_4, \sigma_1^2\sigma_3\sigma_4, \sigma_1\sigma_3^2\sigma_4, \sigma_1\sigma_3\sigma_4^2$ $\sigma_2\sigma_3\sigma_4, \sigma_2^2\sigma_3\sigma_4, \sigma_2\sigma_3^2\sigma_4, \sigma_2\sigma_3\sigma_4^2$ $\sigma_1\sigma_2\sigma_3\sigma_4$

Table 1: Counting and list of monomials appearing in the normalized Hamiltonian \mathcal{K} up to the order $N = 8$ for $n = 3$ et $n = 4$.

4.1.2. Quantum vibrational Hamiltonian

The classical relations between the non-dimensional variables $\{z_j, z_k^*\} = -i\delta_{jk}$, are now replaced by $\frac{1}{i}[\hat{a}_j, \hat{a}_k^\dagger] = -i\delta_{jk}$, i.e.: $1 \leq j, k \leq n$, $[\hat{a}_j, \hat{a}_k^\dagger] = \delta_{jk}$. These operators satisfy the commutation Bose relations and are the boson creation \hat{a}_k^\dagger and annihilation \hat{a}_j operators.

The generators σ_k and the Hamiltonian function \mathcal{K} are correspondingly replaced by the number operators $\hat{N}_k = \hat{a}_k^\dagger \hat{a}_k$, which represent from the physical point of view the number of excitation quanta per oscillator, and Hamiltonian operator \hat{K} . In the development of \hat{K} all the operators are hermitic and the coefficients are real.

4.1.3. Eigenbase of the Hamiltonian \hat{H}_0

The eigenstates of \hat{H}_0 are generated from the empty state by the relation (n_1, n_2, n_3 are the natural integers):

$$\left| n_1, n_2, n_3 \right\rangle = (n_1!n_2!n_3!)^{-\frac{1}{2}} \hat{a}_1^{+n_1} \hat{a}_2^{+n_2} \hat{a}_3^{+n_3} \left| 0, 0, 0 \right\rangle. \quad (14)$$

4.1.4. Numeric simulations

N	Λ	coefficients in cm^{-1}
2	3	$\omega_1 = +739.685, \omega_2 = +1\,245.09$ $\omega_3 = +3\,748.47$
4	9	$\alpha_2^1 = -3.517, \alpha_2^2 = +2.181, \alpha_2^3 = -84.540$ $\alpha_{1,1}^{1,2} = -7.049, \alpha_{1,1}^{1,3} = -0.490, \alpha_{1,1}^{2,3} = -16.291$
6	19	$\alpha_3^1 = -0.259, \alpha_3^2 = -0.778, \alpha_3^3 = -0.173$ $\alpha_{1,2}^{1,2} = -0.131, \alpha_{1,2}^{1,3} = -0.122, \alpha_{1,2}^{2,3} = -3.965$ $\alpha_{2,1}^{1,2} = -0.428, \alpha_{2,1}^{1,3} = -0.508, \alpha_{2,1}^{2,3} = -0.154$ $\alpha_{1,1,1}^{1,2,3} = -0.767$
8	34	$\alpha_4^1 = +0.0098, \alpha_4^2 = +0.0111, \alpha_4^3 = +0.0153$ $\alpha_{3,1}^{1,2} = 0, \alpha_{3,1}^{1,3} = 0, \alpha_{3,1}^{2,3} = +0.0793$ $\alpha_{2,2}^{1,2} = -0.0079, \alpha_{2,2}^{1,3} = -0.0174, \alpha_{2,2}^{2,3} = -0.0426$ $\alpha_{1,3}^{1,2} = +0.0021, \alpha_{1,3}^{1,3} = -0.0007$ $\alpha_{1,3}^{2,3} = +0.2885$ $\alpha_{1,1,2}^{1,2,3} = +0.1553, \alpha_{1,2,1}^{1,2,3} = +0.1003$ $\alpha_{2,1,1}^{1,2,3} = +0.0854$

Table 2: Number of Dunham parameters given by [18]. For the given order N ($4 \leq N \leq 8$), a line contains the number of additional operators with respect to the order $N - 2$.

The vibrational structure of the molecule ClOH has been studied in [18] nearly up to the dissociation limit (the energies are given relative to the $|0, 0, 0\rangle$ ground state located at $2\,867.0\text{ cm}^{-1}$ above the bottom of the potential energy surface. The dissociation energy is $19\,290\text{ cm}^{-1}$). The authors realize a Dunham development of number operators up to the order $N = 8$; such the constructed Hamiltonian allows one to reproduce the vibrational structure of 314 energy levels up to 70 % of the dissociation energy

(i.e. $13\,500\text{ cm}^{-1}$) requiring 34 coefficients which is in accordance with Eq. (11) with the coefficients (enumerated by Eq. (13)) given in Table 2.

5. Conclusion and perspectives

The counting of number operators of an n -degree-of-freedom vibrational non-resonant Hamiltonian, developed in the base of number operators \hat{N}_k up to the given order N , is in a good accordance with the numeric simulations ([18]) for the ClOH molecule. However, with the vibrational levels more strongly excited, one should take into account possible resonances $p : q$ between the different oscillators of the molecular system. In the second article, we complete the method of construction and counting of coupling operators induced by the resonance for the case of one single resonance $p : q$.

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